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**Title:** Probing the Ionic Liquid-Vapor Interface by Ambient Pressure X-ray Photoelectron Spectroscopy

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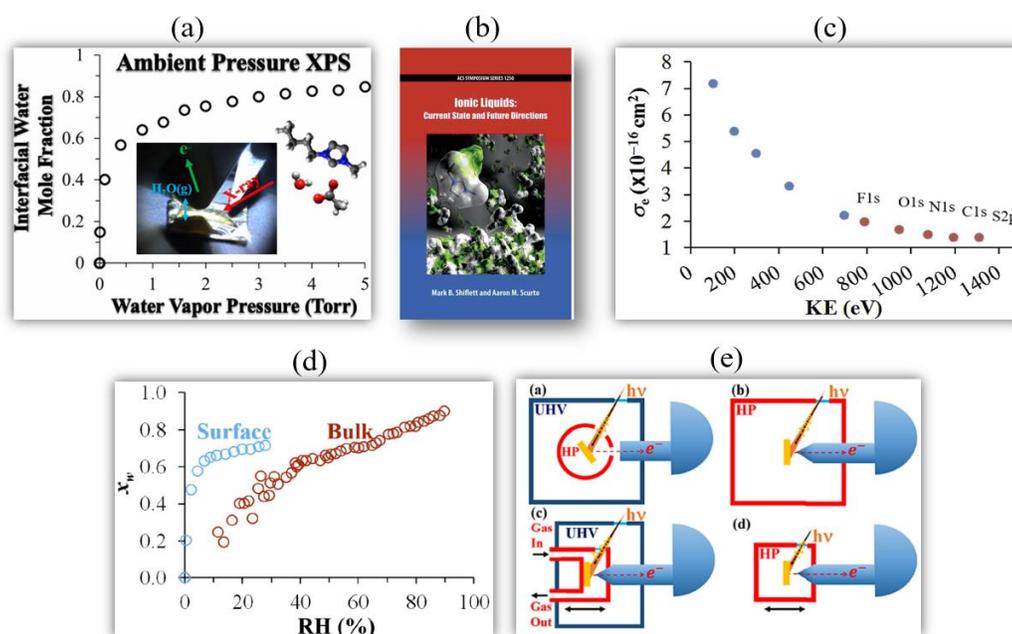
The interaction of ionic liquids (ILs) with small gas phase molecules (CO, CO<sub>2</sub>, H<sub>2</sub> and H<sub>2</sub>O) derived from petroleum-based processes have been studied extensively due to their relevance in separation, catalytic, and electrochemical applications. Many of these applications involve the gas phase species passing through the IL-vapor interface. However, to date very little is known about the molecular level chemistry of the interfacial region of ILs under in situ conditions (in the presence of the vapor). There has been a tremendous amount of effort in the literature to understand IL interfaces using vacuum-based X-ray photoelectron spectroscopy. While this method continues to increase our fundamental understanding of the IL-vacuum interface, little is known about ILs under ambient conditions using photoemission techniques. This is due, in part, to the paucity of ambient pressure photoemission instruments available, and the technological difficulties of performing such experiments at liquid-gas interfaces. The focus of our work has been utilizing a recently commissioned ambient pressure X-ray photoelectron spectroscopy (APXPS) instrument in our laboratory to probe the IL-gas interface under Torr level gas phase pressures. To date this grant has funded three PhD students (Alicia Broderick, Yehia Khalifa and Meng Jia) who have focused on applying APXPS to understand the chemical composition and structure of the IL-gas interface.

Alicia Broderick drove research that lead to the first pressure-dependent APXPS study in the literature of an IL interface by examining the hydrophilic IL 1-butyl-3-methylimidazolium acetate, [BMIM][OAc], in the presence of water vapor (**Fig 1a**).<sup>1</sup> In addition to providing the first quantitative assessment of an adsorbate at the IL-gas interface under ambient conditions, this study also reported observations that the interface undergoes a structural transition above a water mole fraction ( $x_w$ ) of 0.6. These results are consistent with molecular dynamic (MD) simulations that show [BMIM][OAc] undergoing a transition from being a homogeneous IL/water mixture ( $x_w < 0.6$ ) to a system that is composed of nanostructured hydrophilic and hydrophobic regions ( $x_w > 0.6$ ). Alicia was also the primary author on an invited ACS book chapter providing a comprehensive review of experiments and MD simulations examining water at IL-vacuum, IL-gas and IL-solid interfaces (**Fig 1b**).<sup>2</sup> Alicia has also performed pressure and temperature dependent APXPS studies with [BMIM][OAc] in order to extract surface thermodynamics of a gas phase adsorbate at the IL-gas interface. This work is currently being written up.

The second graduate student Yehia Khalifa drove research that examined the IL-water vapor interface of a hydrophobic IL, 1-ethyl-3-methylimidazolium-bis-(trifluoromethylsulfonyl)-imide, [EMIM][Tf<sub>2</sub>N].<sup>3</sup> This unique work allowed for the first kinetic energy dependent electron scattering cross section measurements of a gas phase using photoemission spectroscopy in the absence of variable X-rays (**Fig 1c**). Yehia has also published work that examined water at the IL-gas interface as a function of relative humidity (RH) for 1-hexyl-3-methylimidazolium chloride, [HMIM][Cl].<sup>4</sup> By comparing the observed water mole fraction at the IL-gas interface (via APXPS) to published results of bulk water mole fractions at the same RH, it was found that water is significantly enhanced at the interface relative to the bulk (**Fig 1d**). Yehia has also performed research on IL mixtures containing one cation and two different anions using XPS. This work is also being done in collaboration with theoretical chemists who performed MD simulations. Both XPS and MD show a strong surface enhancement of one anion versus the other. This work is currently submitted for publication.

The third graduate student Meng Jia has built a custom *in-vacuo* 3 electrode setup for the APXPS system to examine the IL-gas interface under the influence of an electrochemical potential. Initial experiments have examined the influence of a bias on photoelectron shifts of [BMIM][OAc] and is currently being written up for publication. This grant also supported Meng as a co-author on a comprehensive review paper on lab-based APXPS (**Fig 1e**).<sup>5</sup>

In summary, in addition to the 5 publications produced to date, an additional 3 publications are in preparation or have been submitted. Both Alicia Broderick and Yehia Khalifa graduated in Summer 2018 with their Ph.D degrees, and Meng Jia is currently driving this IL research working towards his Ph.D.



**Figure 1.** Representative images from work in references (a) 1, (b) 2, (c) 3, (d) 4 and (e) 5.

## References

- (1) Broderick, A.; Khalifa, Y.; Shiflett, M. B.; Newberg, J. T. Water at the Ionic Liquid-Gas Interface Examined by Ambient Pressure X-Ray Photoelectron Spectroscopy. *J. Phys. Chem. C* **2017**, *121*, 7337-7343.
- (2) Broderick, A.; Newberg, J. T. *Water at Ionic Liquid Interfaces in, Ionic Liquids: Current State and Future Directions*, American Chemical Society: Washington, DC, **2017**, p. 227-249.
- (3) Khalifa, Y.; Broderick, A.; Newberg, J. T. Water Vapor Electron Scattering Cross-Section Measurements using a Hydrophobic Ionic Liquid. *J. Electron Spectrosc. Relat. Phenom.* **2017**, *222*, 162-166.
- (4) Khalifa, Y.; Broderick, A.; Newberg, J. Surface Enhancement of Water at the Ionic Liquid-Gas Interface of [HMIM][Cl] Under Ambient Water Vapor. *J. Phys. : Condens. Matter* **2018**, *30*, 325001.
- (5) Arble, C.; Jia, M.; Newberg, J. T. Lab-Based Ambient Pressure X-Ray Photoelectron Spectroscopy from Past to Present. *Surf. Sci. Rep.* **2018**, *73*, 37-57.